# Can a frustrated spin-cluster model describe the low-temperature physics of NaV$_2$O$_5$ ?

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Recent experimental evidence suggest the existence of three distinct V-valence states (V$^{+4}$, V$^{+4.5}$ and V$^{+5}$) in the low-temperature phase of NaV$_2$O$_5$ in apparent discrepancy with the observed spin-gap. We investigate a novel spin cluster model, consisting of weakly coupled, frustrated four-spin clusters aligned along the crystallographic b-axis that was recently proposed to reconcile these experimental observations. We have studied the phase diagram and the magnon dispersion relation of this model using DMRG, exact diagonalization and a novel cluster-operator theory. We find a spin-gap for all parameter values and two distinct phases, a cluster phase and a Haldane phase. We evaluate the size of the gap and the magnon dispersion and find no parameter regime which would reproduce the experimental results. We conclude that this model is inappropriate for the low-temperature regime of NaV$_2$O$_5$.

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*Introduction* Recent investigations of electronically quasi one-dimensional (1D) transition metal compounds probe the limits of our understanding of the interplay between structural and electronic effects in such low dimensional materials. In NaV$_2$O$_5$, a prototypical example for this class of materials, V-ions are arranged in ladders along the crystallographic b-direction. Measurements of the magnetic susceptibility [4] in the high-temperature phase indicate the presence of only one equivalent V-site [1,2] with valence V$^{+4.5}$, consistent with a model where the electrons in bonding V-O-V orbitals along the rungs of the ladder form a 1D Heisenberg chain [1,3].

At $T_C = 34$ K the unit-cell doubles along the a- and b- and quadruples along the c-axis [5] in a phase transition of as-of-yet unknown origin. At the same time a spin-gap of $\Delta_{min} = 10$ meV opens [4] and charge ordering $2V^{+4.5} \rightarrow V^{+4} + V^{+5}$ sets in [6]. The observed charge ordering is inconsistent with a generic spin-Peierls scenario [4] and raises the question about the driving force (lattice, magnetic or Coulomb) responsible for this transition. Since NaV$_2$O$_5$ is an insulator, the discussion of the material is simplified by the introduction of pseudospins for the charge degrees of freedom that couple to the spin-degrees of freedom [7–10]. The effective spin-Hamiltonian depends, consequently, on the pattern of charge order [11] and may differ in the high- and the low-temperature phase.

The occurrence of two well defined magnon-branches for $T < T_C$ in NaV$_2$O$_5$ along the $a$ direction (perpendicular to the chains), as measured by neutron scattering [16], had been explained tentatively by a model, where the charge orders in a 'zig-zag' pattern in the low-temperature phase [11]. This proposal has been questioned by recent analysis of the low-temperature crystal structure [12,13]. Based on bond-charge models, the existence of three different V-valence states (V$^{+4}$, V$^{+4.5}$ and V$^{+5}$) has been proposed [15,13], as illustrated in Fig. 1. In this analysis, pairs of V$^{+4.5}$ form dimerized spin-chains on every other ladder, which alone could explain the observed spin-gap [11]. A puzzle is posed however, by the presence of free isolated moments on the V$^{+4}$ ions on the remaining ladders, which is inconsistent with the existence of such a gap.

As one possible reconciliation, Boer *et al.* [13] recently proposed that the V$^{+4}$ moments are quenched by their interaction with the neighboring V$^{+4.5}$ sites of the adjacent dimerized V-O-V ladder. Within this model, clusters of six Vanadiums each (and with four spins) would be weakly coupled and the observed spin-gap would arise not from the dimerization but locally from the gap of the isolated clusters.

To distinguish between these fundamentally different mechanisms we study this model by a series of complementary approaches, using DMRG [14], exact-diagonalization and a novel bond-cluster theory, to map all physically relevant regions of its phase diagram. We find that the ground state varies continuously from a cluster-phase for large $J'$ to a Haldane-phase for small $J'$ (see Fig. 1). We evaluate the gap and the dispersion and find that there is no parameter regime that would explain the neutron-scattering data [16].

*The spin-cluster model* We denote by $\mathbf{S}_{n,i}$ ($i = 1, \ldots, 4$) the four spins of the $n$'th cluster, compare Fig. 1. The Hamiltonian is then

$$H = J_1 \sum_n \mathbf{S}_{n,1} \cdot \mathbf{S}_{n,2} + J_2 \sum_n \mathbf{S}_{n,1} \cdot \mathbf{S}_{n+1,2}$$

$$+ J' \sum_n (\mathbf{S}_{n,1} + \mathbf{S}_{n,2}) \cdot (\mathbf{S}_{n,3} + \mathbf{S}_{n,4}) \ , \qquad (1)$$

where $J_1 = J(1 + \delta)$ and $J_2 = J(1 - \delta)$ (with $J_1, J_2, J' > 0$). $\delta$ is the degree of dimerization. For $J' = 0$ the $\mathbf{S}_{n,1/2}$ form a dimerized chain with an in-chain gap $\sim J\delta^{2/3}$. A particular property of Eq. (1) is the local coupling to the

total spin $\mathbf{S}_{n,3} + \mathbf{S}_{n,4}$, which is consequently a (locally) conserved quantity, $(\mathbf{S}_{n,3} + \mathbf{S}_{n,4})^2 = S_n(S_n + 1)$ for any $n$. In the ground-state $S_n \equiv 1$.
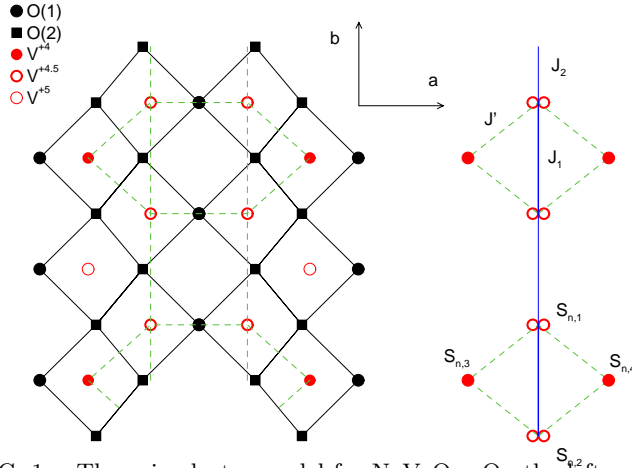


FIG. 1. The spin-cluster model for $NaV_2O_5$. On the left the charge valency in one V-O plane obtained from two crystal structure determinations [15,13]. On the right the proposed cluster spin-model [13]. Note, that two $V^{+4.5}$ on one rung share one electron.

We consider first an isolated cluster and denote by $s_{ij}$ and $t_{ij}^{\alpha}$ the wavefunctions of the singlet and of the triplets ($\alpha = -1, 0, +1$) of the spins $i$ and $j$ ($i, j = 1, \ldots 4$,). The low-energy states are

$$\psi_1 = \frac{1}{\sqrt{3}} \left[ t_{12}^0 t_{34}^0 - t_{12}^+ t_{34}^- - t_{12}^- t_{34}^+ \right] \ , \tag{2}$$

$$\psi_2 = s_{12} s_{34}, \qquad \psi_3^{\alpha} = s_{12} t_{34}^{\alpha} \ , \tag{3}$$

$$\psi_4^0 = \frac{1}{\sqrt{2}} \left[ t_{12}^+ t_{34}^- - t_{12}^- t_{34}^+ \right] \ , \tag{4}$$

where $\psi_4^0$ is the $S^z = 0$ component of the triplet $\psi_4^{\alpha}$. The corresponding energies are $E_1 = -2J' + J_1/4$, $E_2 = E_3 = -3J_1/4$ and $E_4 = -J' + J_1/4$ [17].

For $J'/J_1 > 0.5$ the singlet $\psi_1$ is the ground-state (we denote this region the 'cluster phase'). For $J'/J_1 < 0.5$ the ground-state of the isolated cluster is four-fold degenerate, the singlet $\psi_2$ and the triplet $\psi_3$ have the same energy. Note that the intercluster coupling $J_2$ will not mix $\psi_2$ and $\psi_3$, since the local spin $\mathbf{S}_{n,3} + \mathbf{S}_{n,4}$ is conserved. Intercluster coupling $J_2$ will lead to an antiferromagnetic interaction $J_H \sim (J' J_2)^2/J_1^3$ between the moments of the $\psi_3$ states, as can be evaluated easily in second-order perturbation in $J_2$ (using the complete set of eigenstates of the cluster). The total energy is therefore lowered by $J_2$ when all cluster states are $\psi_3$. The $S = 1$ moments of the $\psi_3$ states thus form an effective spin-1 chain with a Haldane gap $\Delta_H = 0.41050 J_H$ [18]. We denote this region therefore the 'Haldane phase'.

We have evaluated the energy gap of the spin-cluster model by DMRG [14], using the finite-size algorithm with open boundary conditions for systems with $L = 32$ and $L = 64$ spins. The ground-state has $N_{\uparrow} = L/2$ up-spins and $N_{\downarrow} = L/2$ down-spins. We retained typically 60 states of the density matrix, checking the convergence by additional calculations with 40 and 90 states respectively. We evaluated the gap by two complementary methods, namely (i) by targeting two states in the sector with $N_{\uparrow} = L/2 = N_{\downarrow}$ and (ii) by targeting the ground states in (a) the sector with $N_{\uparrow} = L/2 = N_{\downarrow}$ and (b) $N_{\uparrow} = L/2+1$ and $N_{\downarrow} = L/2 - 1$. We find complete consistency and present the results in Fig. 2 for some selected values for the dimerization $\delta$. The finite-size corrections are smaller than the symbol sizes. We find a rapidly decreasing gap as a function of decreasing $J'/J$ and a smooth crossover between the cluster- and the Haldane phase. As the symmetry of these two phases is the same, we do not expect a phase transition in the thermodynamic limit.
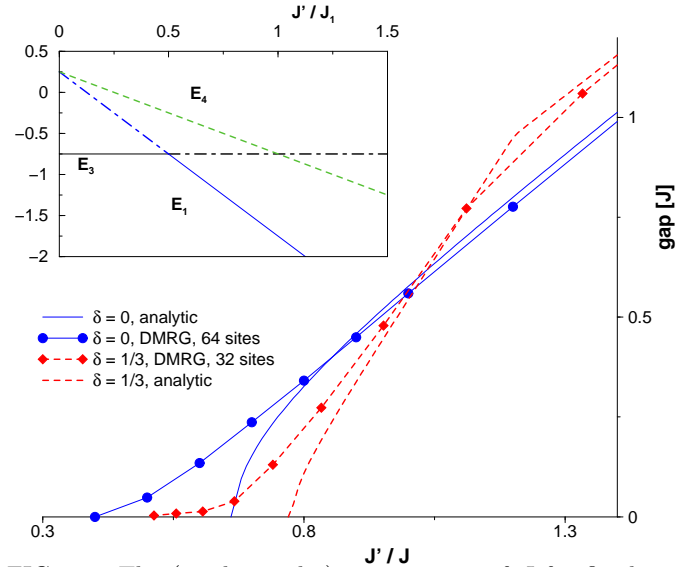


FIG. 2. The (singlet-triplet) gap in units of $J$ for fixed $\delta = 0$ and $\delta = 1/3$ as a function of $J'$. Filled Symbols: DMRG data. Lines: Results from the cluster operator theory. Inset: The three low-lying energy levels $E_1$, $E_3$ and $E_4$ for an isolated cluster in units of $J_1$ as a function of $J'/J_1$. The corresponding wavefunctions $\psi_3^{\alpha}$ and $\psi_4^{\alpha}$ are triplets, $\psi_1$ is a singlet.

*Cluster-operator theory* In the cluster-phase two low-lying triplet modes, $\psi_3^{\alpha}$ and $\psi_4^{\alpha}$, are relevant. In order to take the effect of the intercluster coupling $J_2$ into account we describe the seven degrees of freedom of cluster $n$ by bosonic degrees of freedom: $s_n^{\dagger}$ for the singlet ($\psi_1$) and $b_{n,3,\alpha}^{\dagger}$ and $b_{n,4,\alpha}^{\dagger}$ for the triplets ($\psi_3$ and $\psi_4$). The low-lying singlet $\psi_2$ does not couple and may be disregarded here. This approach generalizes the bond-operator theory for dimerized spin-chains [19] to the case of spin-clusters.

The constraint $s_n^\dagger s_n + \sum_{\tau,\alpha} b_{n,\tau,\alpha}^\dagger b_{n,\tau,\alpha} = 1$ $(\tau = 3,4)$ restricts the bosonic Hilbert space to the physical one. The spin-operators take the form

$$S_{n,1/2}^z = \pm \frac{b_{n,3,0}^\dagger s_n + s_n^\dagger b_{n,3,0}}{\sqrt{12}} - \frac{b_{n,4,0}^\dagger s_n + s_n^\dagger b_{n,4,0}}{\sqrt{6}} \;. \quad (5)$$

Note, that there are no terms $\sim b_{n,\tau,\alpha}^\dagger b_{n,\tau',\alpha'}$ corresponding to triplet-triplet interactions. In linearized Holstein-Primakov approximation (LHP), we substitute $s_n^\dagger \to 1$ and $s_n \to 1$ in Eq. (5) and in similar expressions for $S_{n,1/2}^{x/y}$. This approximation retains spin-rotational invariance and we may disregard the index $\alpha = -1,0,1$ for the triplet operators. We obtain for the LHP Hamilton-operator in momentum space $H^{(LHP)} = H_0 + H_2^{(1)} + H_2^{(2)}$ with $H_0 = \sum_{k,\tau} \Delta_\tau b_{k,\tau}^\dagger b_{k,\tau}$ $(\Delta_\tau = E_\tau - E_1)$. The inter-cluster coupling is given by
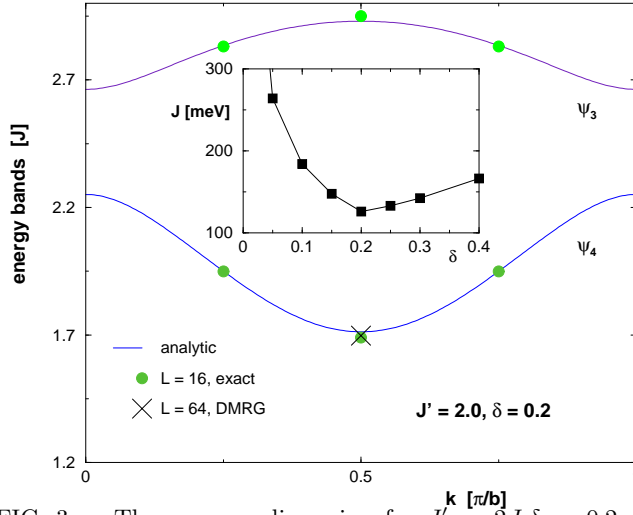


FIG. 3. The magnon dispersion for $J' = 2J, \delta = 0.2$. Note the zero of energy. The lines are the result of the cluster-operator theory, the circles of an exact diagonalization study with 16 spins (periodic boundary conditions). The cross denotes the DMRG result. Inset: The value of $J$ as a function of dimerization $\delta$ needed to fit the measured dispersion of NaV$_2$O$_5$ (LHP result, for $J/2 < J' < J$).

$$H_2^{(1)} = \frac{J_2}{12} \sum_k \left[ 2\cos(2bk)\left(2b_{k,4}^\dagger b_{k,4} - b_{k,3}^\dagger b_{k,3}\right)\right.$$

$$\left. + i2\sqrt{2}\,\sin(2bk)\left(b_{k,3}^\dagger b_{k,4} - b_{k,4}^\dagger b_{k,3}\right)\right] \quad (6)$$

and

$$H_2^{(2)} = \frac{J_2}{12} \sum_k \left[ \cos(2bk)\left(2b_{-k,4}^\dagger b_{k,4}^\dagger - b_{-k,3}^\dagger b_{k,3}^\dagger\right)\right.$$

$$\left. - i2\sqrt{2}\,\sin(2bk)\,b_{k,4}^\dagger b_{-k,3}^\dagger \; + \; \text{h.c.}\right] \;. \quad (7)$$
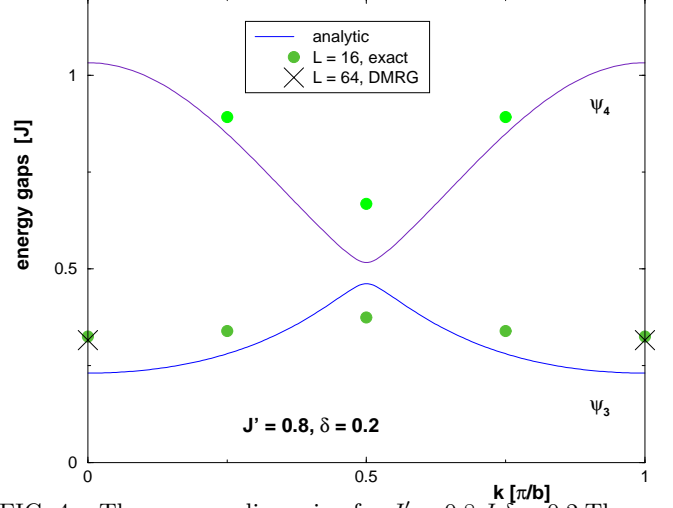


FIG. 4. The magnon dispersion for $J' = 0.8\,J, \delta = 0.2$. The symbols as in Fig. 3. Note that the cluster-operator theory overestimates the magnon-dispersion.

Here $b = 3.611$ Å is the lattice constant of the high-temperature phase. Note the opposite sign in the dispersion of two triplets. It is straightforward to diagonalize $H^{(LHP)}$. We define $c = (J_2/6)\cos(2bk)$, $2t = \Delta_4^2 + \Delta_3^2 + 2c(2\Delta_4 - \Delta_3)$ and $s = \Delta_3^2\Delta_4^2 + 2c\Delta_3\Delta_4(2\Delta_3 - \Delta_4) - 2\Delta_3\Delta_4 J_2^2/9$. The dispersion $\omega_\pm = \omega_\pm(k)$ of the two magnon branches (each branch is three-fold degenerate) in LHP-approximation is then

$$\omega_\pm^2 = t \pm \sqrt{t^2 - s} \;. \quad (8)$$

We have included the results for the magnon gap in Fig. 2. For large ratios $J'/J$ the LHP-result becomes asymptotically exact, in this limit it is equivalent to perturbation theory in $J_2$. In the LHP-approximation the transition to the Haldane phase is signaled by a vanishing of the energy gap, the crossover cannot be described by the cluster-operator theory.

In Fig. 3 we present the magnon-dispersion Eq. (8) for $J' = 2J$ and compare the LHP-results (lines) with an exact-diagonalization study of a system with 16 sites (filled circles) [20]. The agreement is very good, due to the large gap and (correspondingly) small correlation length. Note that the low-lying magnon, which corresponds to $\psi_4$ (see inset of Fig. 2), has its minimum at $k = \pi/(2b)$.

In Fig. 4 we present the magnon-dispersion Eq. (8) for $J' = 0.8J$ which is closer to the transition to the Haldane phase. The agreement with the exact diagonalization and the DMRG data is not good, since the precursors to the Haldane phase are not included in the cluster-operator theory. The low-lying magnon, which corresponds to $\psi_3$ (see inset of Fig. 2), has its minimum now at $k = 0$ and $k = \pi/b$ and a maximum at $k = \pi/(2b)$, as measured by neutron scattering [16]. The cluster-operator theory substantially overestimates the size of the magnon dis-

person relative to the exact-diagonalization result near to the Haldane phase. The physical reason for this discrepancy can be understood: The lattice constant of the effective spin-1 chain in the Haldane phase is $2b$ and the minimum of the magnon dispersion is therefore at $\pi/(2b)$ in the Haldane phase [21]. It changes therefore at the crossover from the cluster phase and the Haldane phase. This change in the location of the gap is not included in the cluster-operator theory.

*Discussion* The exchange constant along $b$ is $J \approx 529 - 560\,\text{K}$ [4,22] in the high-temperature phase of $NaV_2O_5$ and the inter-ladder coupling is probably very small, a $J'/J \approx 1/45$ has been found in an analysis of the magnon-dispersion for $T < T_C$ in a model with zig-zag charge order [11]. This small ratio is consistent with the very small coupling along $a$ found in a LDA-study [1]. There are, however, two reasons why $J'$ might be larger in the low-temperature phase. (a) As noted by Mack and Horsch [3], there is a near cancellation for $T > T_C$ in between paths with intermediate singlet and triplet states and energies $E_{s/t}$: $J' = t_{xy}^2(1/E_s - 1/E_t)$, where $t_{xy}$ is the V-V hopping matrix element in $a$ direction. A corresponding calculation for $T < T_C$ in the phase shown in Fig. 1 yields $J' = 2t_{xy}^2(1/E_s + 1/U - 1/E_t)$ ($U$ is the onsite Hubbard-$U$). (b) $t_{xy}$ might be substantially larger in the low-temperature phase, since the smallness of $t_{xy}$ for $T > T_C$ is a subtle band-structure effect [1]. We have therefore scanned the complete phase diagram of the spin-cluster Hamiltonian in order to determine whether there exists a parameter range able to fit the neutron scattering data.

We have tried to reproduce, within the spin-cluster model, four known properties of $NaV_2O_5$: (i) The gap (averaged over $k_a$) is $\Delta_{min} = 10\,\text{meV}$. (ii) The maximum of the dispersion of the lowest magnon branch is at $\pi/(2b)$, the minimum at $0$ and $\pi/b$. (iii) The value of the maximum of the dispersion of the lowest magnon branch is $\Delta_{max} \approx 40\,\text{meV}$ [16,23], i.e. the ratio is $\Delta_{max}/\Delta_{min} \approx 4$. (iv) The value of the coupling along $b$ is $J \approx 441\,\text{K} = 38\,\text{meV}$ for $T < T_{SP}$ [16,24].

Condition (ii) implies that only the cluster-phase of Hamiltonian Eq. (1) with $J' < J_1$ is a candidate for the low-temperature phase of $NaV_2O_5$. This implies $J_1/2 < J' < J_1$. Within the cluster-operator theory one obtains $\Delta_{max}/\Delta_{min} = 4$ for values of $J'$ near to the gap closing. One needs consequently large coupling constants $J$ (see inset of Fig. 3). in order to reproduce $\Delta_{min} = 10\,\text{meV}$. We have evaluated the values of $J'$ and $J$ needed to reproduce the gap-ratio as a function of dimerization $\delta$ and find a minimum in $J$ for $\delta = 0.2$ (see inset of Fig. 3). This minimum is $J \approx 126\,\text{meV}$, substantially larger than the experimental value $J \approx 38\,\text{meV}$. Note, that the cluster-operator theory overestimates the dispersion in this phase and **underestimates** the value of $J$ needed. We therefore conclude safely, that the model is not able to reproduce the measured magnon-dispersion

of $NaV_2O_5$ and that Eq. (1) is unlikely to be the appropriate model for the low-temperature phase of $NaV_2O_5$, at least in its one-dimensional version. It might be possible, in principle, that two-dimensional couplings change the scenario obtained in the present study, though we note, that an increase in dimensionality does, in general, reduce the size of a spin-gap.

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